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EPR AND FTIR STUDY OF METALS IN BITUMEN AND MINERAL COMPONENTS OF
CIRCLE CLIFFS, UTAH TAR SAND

By

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INTRODUCTION

The presence of certain metals in oil extracted from tar sands can have undesirable catalytic effects on refining and combustion. The cumulative effect of some of these metals on refining makes even trace amounts a serious problem. The technique of electron paramagnetic resonance (EPR) provides a sensitive means of detecting metal ions which exhibit the property of paramagnetism such as V^{4+} , Mn^{2+} and Fe^{3+} .

Numerous authors (1-4) have applied the technique to petroleum and observed an EPR spectrum which they attribute to the paramagnetic vanadium ion V^{4+} in the form of the vanadyl cation VO^{2+} bound in a porphyrin complex. Similar spectra have been observed for tar sand samples from the Athabasca deposit in Alberta, Canada (5, 6). Vanadium concentrations in various U. S. tar sands have been investigated by Branthaver and Dorrence (7) using optical colorimetry and UV spectroscopy. Using EPR on a tar sand sample from the P. R. Spring outcrop in Utah, Malhotra and Graham (8) have shown that no vanadium is present in the organic fraction in the V^{4+} state, but that there is inorganically bound vanadium in the clay fraction. This is consistent with the findings of Branthaver and Dorrence (7).

In the present study, the EPR technique has been applied to a tar sand sample originating from Circle Cliffs, Utah which, like P. R. Spring, is also one of the areas from which samples were taken for the Branthaver and Dorrence study (7). For Circle Cliffs, they reported the organic fraction to contain some vanadium but none that was porphyrin-bound.

PROCEDURE

The tar sand sample (USBM-3851) was separated into various fractions by Soxhlet extraction using the method described in (9). The whole tar sand was separated into an organic fraction (bitumen) and an inorganic fraction (mineral matter) using benzene. The bitumen was further separated using heptane into a heavy end fraction (asphaltene) and a light end fraction (petroleum).

EPR measurements were made by placing the various fractions into 3 mm O.D. quartz sample tubes in a rectangular TE_{102} mode cavity of a 9.1 GHz (Varian V-4500) spectrometer with 100 kHz magnetic field modulation.

The mineral matter was dried in an oven at $110^{\circ}C$ for several hours. Fourier transform infrared (FTIR) spectra of this fraction were obtained by grinding a small sample of mineral with KBr in a 1:100 ratio (by weight) using a Wig-L-Bug, pressing the mixture into a pellet and scanning with a Nicolet 5-DXE FTIR spectrometer.

RESULTS AND DISCUSSION

The EPR spectrum of the asphaltene is shown in Figure 1. Aside from the strong free radical signal at $g=2.00$ common to all asphaltenes, the only other feature is a powder pattern spectrum characteristic of an ion with an electronic spin $S=1/2$ and a nuclear spin $I=7/2$, located at a site with axial symmetry. The spin Hamiltonian describing such a system is

$$H = g_{\parallel} \beta S_z H_z + g_{\perp} \beta (S_x H_x + S_y H_y) + A_{\parallel} S_z I_z + A_{\perp} (S_x I_x + S_y I_y) \quad (1)$$

g_{\parallel} and g_{\perp} are the components of the g -factor parallel and perpendicular to the symmetry axis Z and A and A are the corresponding components of the hyperfine splitting constant. The second order solution giving the line positions are

$$H_{||} (m) = H_{||} - \frac{A_{||}}{g_{||}\beta} m - \frac{A_{\perp}^2}{2H_{||} (g_{||}\beta)^2} [I(I+1) - m^2] \quad 2)$$

for

$$H_{\perp} (m) = H_{\perp} - \frac{A_{\perp}}{g_{\perp}\beta} m - \frac{A_{||}^2 + A_{\perp}^2}{4H_{\perp} (g_{\perp}\beta)^2} [I(I+1) - m^2] \quad 3)$$

The line positions measured from the spectrum in Figure 1 were fitted to Equations 2 and 3 and the values of the spin Hamiltonian determined. They are listed in Table I along with EPR data on several synthetic vanadyl porphyrins. A comparison indicates that the source of the EPR spectrum is vanadyl etioporphyrin. Etioporphyrin is one of the most common porphyrins found in tar sands, oil shale and petroleum (15).

TABLE I

EXPERIMENTAL EPR PARAMETERS FOR VARIOUS VANADYL PORPHYRINS

Complex	$g_{ }$	g_{\perp}	$A_{ }$ (mT)	A_{\perp} (mT)	Reference
Circle Cliffs asphaltene	1.962 (3)	1.986 (1)	17.20 (8)	6.08 (6)	Present work
VO Etioporphyrin	1.9629	1.9862	17.13	6.01	10
VO Porphin in triphenylene	1.964	1.985	17.4	5.9	11
VO Mesoporphyrin dimethyl ester	1.947	1.988	15.8	5.4	12
VO Octamethyltetraazaporphyrin	1.944	1.980	16.3	5.8	11
VO Tetrabenzoporphyrin	1.962	1.985	15.0	5.0	11
VO Tetrapyrildiporphyrin	1.961	1.984	15.7	5.4	11
VO Tetraphenylporphyrin	1.961	1.986	16.0	5.7	13
VO Phthalocyanine	1.966	1.989	15.8	5.6	11

There are at least two possible explanations for the detection by EPR of a vanadyl porphyrin in Circle Cliffs tar sand in the present study when it remained undetected in the earlier work (7). First, the porphyrin content may be quite variable in the Circle Cliffs deposit. Secondly, UV spectroscopy is not as intrinsically sensitive as the EPR technique. In a recent study, Shultz and Selucky (6) have applied both methods to samples of Athabasca tar sand and found that they could observe the 410 nm Soret band characteristic of vanadyl porphyrins, in fractions in which high concentrations of V^{4+} were detected by EPR; however, in fractions with low vanadyl porphyrin concentrations (as determined by the V^{4+} EPR signals), no optical absorption could be observed.

In order to obtain a powder pattern spectrum of the petrolene which is a viscous fluid, it was necessary to solidify the sample at -20°C . The EPR spectrum of the fraction also indicates the presence of vanadyl etioporphyrin.

Figure 2 shows the EPR spectrum of the mineral matter at $g \approx 2.0$. Of interest are the 6 intense, broad lines (labelled I) and the 6 intense, sharp lines (labelled II). The average hyperfine splitting of the two series is ≈ 9.3 mT which is characteristic of Mn^{2+} ($S=5/2$, $I=5/2$) in the tetragonal symmetry of a carbonate lattice (16). The carbonates common to the minerals associated with tar sands are calcite, dolomite, magnesite, aragonite and rhodochrosite. The last two can be eliminated from the list of candidates since their spectra do not show any hyperfine splitting. Of the three remaining possibilities, an FTIR analysis of the mineral matter shows dolomite to be the most likely.

Figure 3 shows the FTIR spectrum of the mineral fraction and the spectrum of dolomite for comparison. As can be seen, the characteristic broad line at 1441 cm^{-1} and the two sharp lines at 880 and 729 cm^{-1} indicate that dolomite is one of the components of the mineral matter. Absent, however, are the characteristic lines of calcite at 1429 , 876 and 710 cm^{-1} and of magnesite at 1449 , 885 and 746 cm^{-1} (17).

The appropriate spin Hamiltonian for Mn^{2+} at a tetragonal site in carbonates is

$$H = g\beta H \cdot S + D[S_z(S+1)] + A S_z I_z \quad 4)$$

where D is the zero field splitting constant. Since there is significant disagreement in the literature between the values of g, A and D reported for single crystal dolomite (18, 19) and those

obtained for polycrystalline samples (20), we have derived a revised set of EPR parameters for a sample of dolomite for comparison with the tar sand mineral fraction spectrum.

The powder pattern spectrum of a polycrystalline dolomite sample from the Arbuckle Mountain Range in Oklahoma was recorded and is shown in Figure 4a. The observed spectrum is actually a superposition of two spectra due to Mn^{2+} occupying two inequivalent sites in the $MgCa(CO_3)_2$ crystal lattice. The six more intense lines labelled "Mg" in Figure 4a, are the allowed ($\Delta m=0$) transition lines for Mn^{2+} substituted at Mg sites and the six less intense lines labelled "Ca", are the allowed lines for Mn^{2+} at Ca sites (18-20).

The computer simulation shown in Figure 4b was calculated for the allowed transitions using a third order solution of the spin Hamiltonian derived by De Wijn and Van Balderen (21) for line positions and an equation derived by Allen (22) for the line intensities. As can be seen by comparison with Figure 4a, agreement with the observed spectrum is very good with line positions reproduced to within ± 0.07 mT. The values thus obtained for the EPR parameters are given in Table II.

TABLE II
EPR PARAMETERS FOR Mn^{2+} IN VARIOUS CARBONATES AND IN THE
MINERAL FRACTION OF CIRCLE CLIFFS TAR SAND

Sample	g	A (mT)	Δ (mT)	Reference
Mineral Matter I	2.003 \pm .001	-9.26 \pm .01	14.8 \pm .3	Present work
Mineral Matter II	2.003 \pm .001	-9.48 \pm .01	---	Present work
Dolomite Mg site	2.0028 \pm .0001	-9.27 \pm .01	14.60 \pm .05	Present work
Dolomite Ca site	2.0028 \pm .0001	-9.48 \pm .01	---	Present work
Calcite	2.002 \pm .001	-9.55 \pm .05	8.0 \pm .1	(24)
Magnesite	2.0018 \pm .0006	-9.22 \pm .01	9.0 \pm .1	(20)

The spectrum of the mineral matter fraction of the tar sand sample (Figure 2) is complicated by severe broadening and overlap; however, values of the magnetic parameters g, and A, have been obtained by fitting the peak line positions to the third order solution (21). D was obtained using the equation by Bleaney and Rubins (23)

$$\delta H = x \left[z + \frac{y^2}{4(y+z)} \right] \quad 5)$$

where

$$\begin{aligned} x &= 2D^2/g\beta H \\ y &= 8(1-9m/g\beta H) \end{aligned} \quad 6)$$

and

$$z = 1 + Am/g\beta H$$

which gives the splitting δH , between the main allowed transition lines and their corresponding "anomalous" lines in the powder pattern. The value of D for Mn^{2+} at an mg-site is such that only two anomalous lines can be observed (labelled "A" in Figure 4a); in the case of the mineral matter, because of severe broadening and overlapping, only one line is resolved (labelled "A" in Figure 2).

The values of the EPR parameters derived from the mineral matter spectrum are given in Table II together with results for magnesite, calcite and dolomite for comparison. It is obvious from the data that the spectrum can only be that of Mn^{2+} in dolomite with the lines designated as I and II corresponding to substitutions at Mg and Ca sites, respectively.

Another feature in the mineral matter spectrum is a line at $g=4.2$, shown in Figure 5. This is characteristic of Fe^{3+} which in this case is probably located at a site in clay.

CONCLUSIONS

The results of this study suggest that EPR, supplemented by FTIR, is a particularly sensitive technique in the identification and characterization of paramagnetic metal ions in the complex mixture of organic and mineral matter comprising tar sands. As demonstrated in the present work, EPR has the additional advantage of permitting a determination of the site of metals, either

EPR SPECTRUM OF
CIRCLE CLIFFS ASPHALTENE

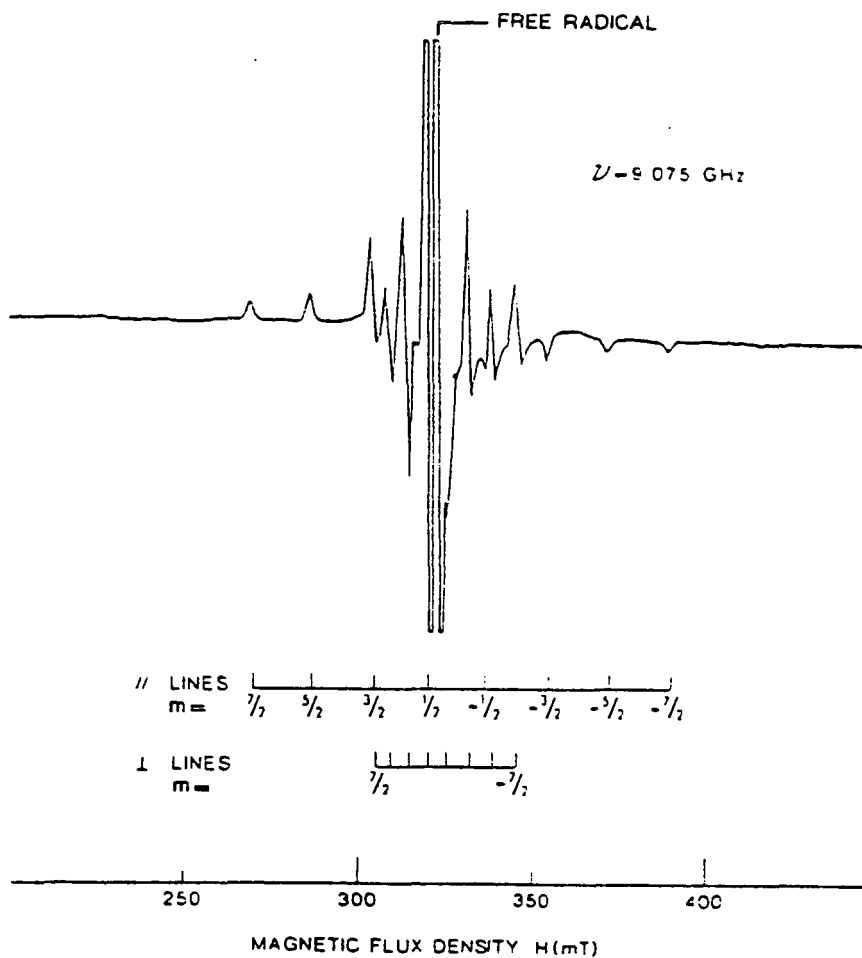


Figure 1. EPR spectrum of Circle Cliffs tar sand asphaltene.

CIRCLE CLIFFS MINERAL MATTER : HIGH FIELD

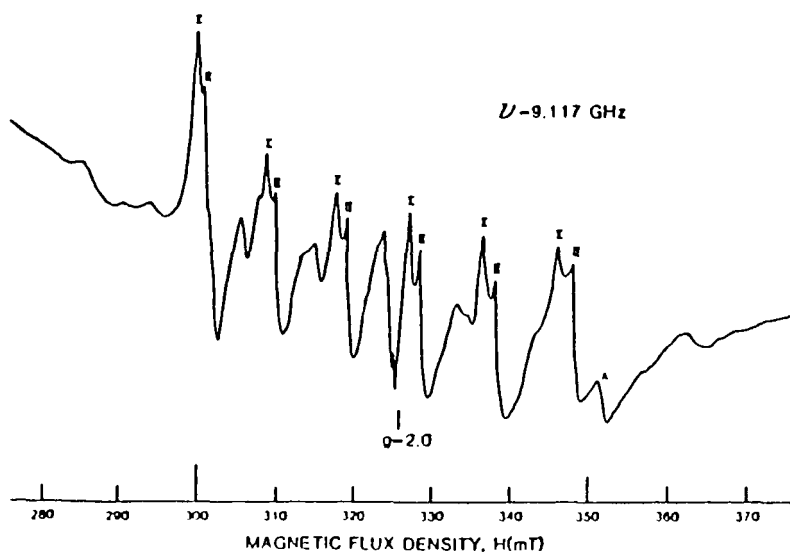


Figure 2. EPR spectrum of Circle Cliffs tar sand mineral matter at $g \approx 2$.

FTIR SPECTRUM OF (A) MINERAL MATTER (B) DOLOMITE.

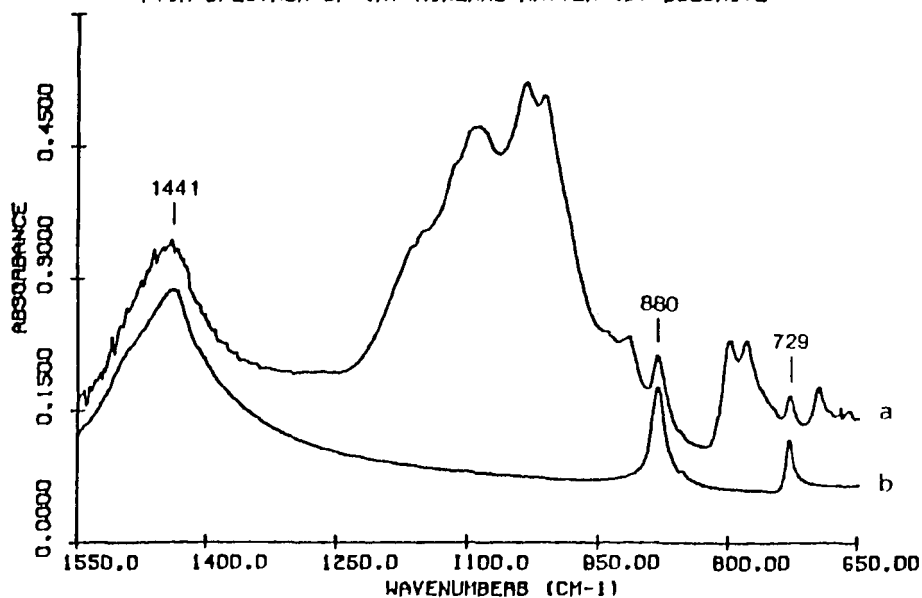


Figure 3. FTIR spectrum of (a) Circle Cliffs tar sand mineral matter (b) dolomite.

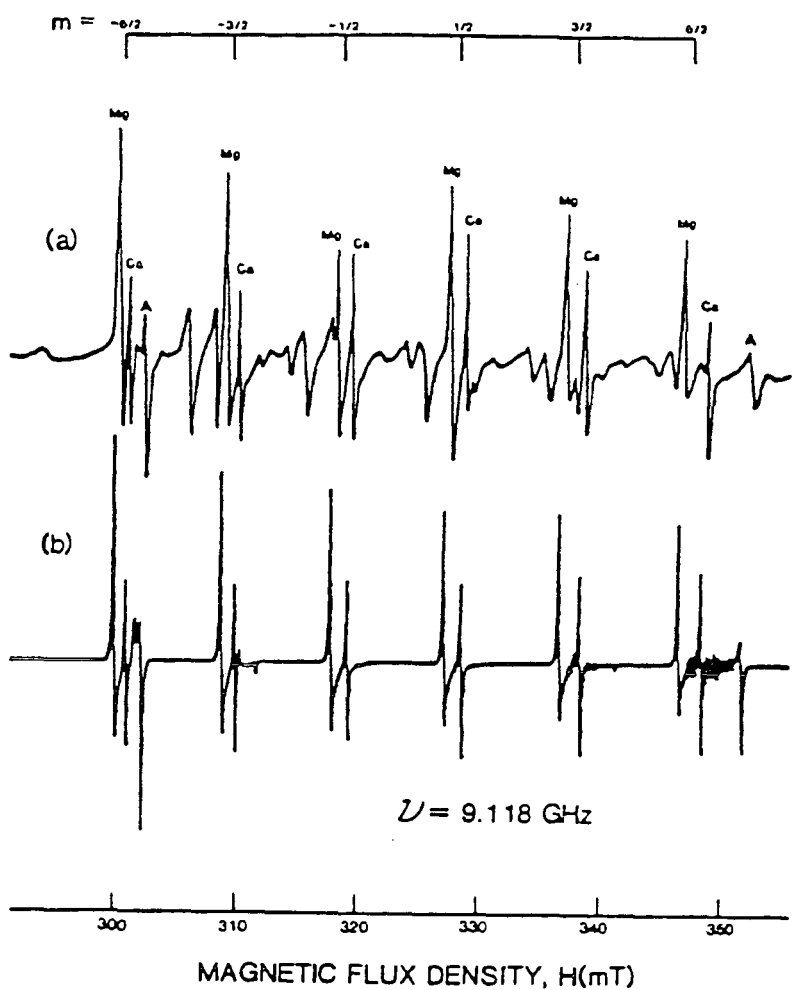


Figure 4. (a) EPR spectrum of polycrystalline dolomite. (b) simulation of (a).

CIRCLE CLIFFS MINERAL MATTER : LOW FIELD

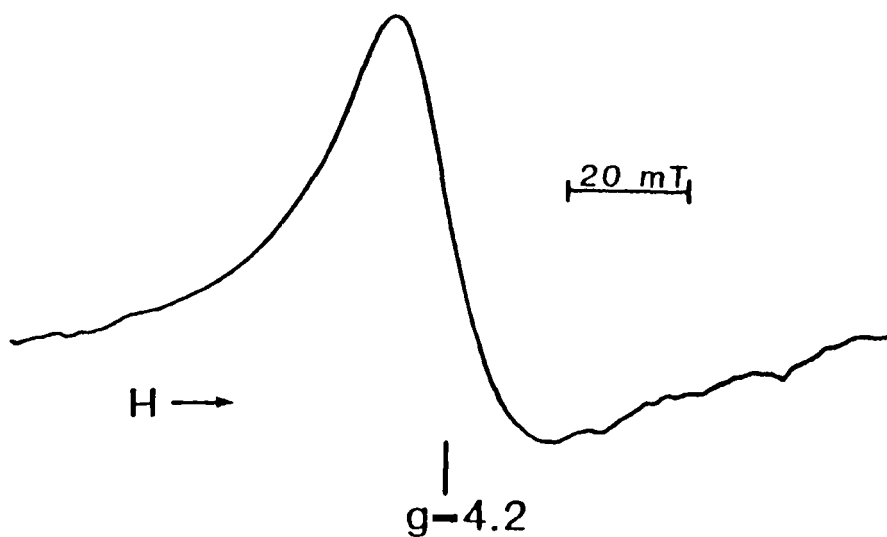


Figure 5. EPR spectrum of Circle Cliffs tar sand mineral matter at $g \approx 4$.

occurring in minerals or bound in organic complexes. This may be particularly useful when the mineral phase and bitumen are not readily separable and their interactions have consequences for recovery processes (9).

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